SPECIFICATION

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PULSED ELECTRON JUMP GENERATOR

Cross Reference to Related Applications

This is a continuation-in-part of Application No. 09/589,669 filed June 7, 2000 which is a divisional application of Application No. 09/304,979 filed May 4, 1999, now U.S. Patent No. 6,114,620.

Background of Invention

[0001]   The present invention relates generally to converting energy into useful forms, and particularly, to converting energy into useful forms by stimulating high peak reaction rates of short duration in chemical reactions in a regional volume.

[0002]   A method to convert chemical energy into electricity uses chemical reactions such as fuel-air reactions to create non-equilibrium concentrations of highly vibrationally excited products. When those products migrate to a conducting surface, the products may generate hot electrons in the surface. When the conducting surface is sufficiently thin, a form of semiconductor device may collect the hot electrons and convert them into electricity.

[0003]   Another method to convert chemical energy into electricity uses chemical reactions such as a fuel-air reaction to create photon radiation with energies characteristic of the reaction temperatures. Because the photon energies of typical reaction temperatures lie within the range of photovoltaic semiconductor converters, photons may be converted into electricity using photovoltaic means. A portable thermo-photovoltaic power source is described in the U.S. Patent No. 5,593,509.

[0004]   The efficiency of a known device that stimulates reactions increases with the temperature of the device. The efficiency of the device to collect and convert the

reactants to electricity, however, decreases sharply as the operating temperature increases beyond ambient temperature, which for typical semiconductors is about 300 to 400 degree Kelvin.

[0005]   It is, therefore, highly desirable to operate an energy collecting and converting device at an ambient temperature while operating the chemical reactions that generate vibrationally excited specie at the maximum possible temperature and reaction rate.

[0006]   Pulsed chemical reactions cause maximum reaction rate and permit a device, e.g., a semiconductor device, to operate up to its highest allowable operating temperature. The thermal mass of the semiconductor delays and minimizes significant heating. During the period of time between pulses, also referred to as a dead time, the energy collecting device may dissipate the heat generated during the pulsed reaction time and peak power portion of the reaction-collection cycle.

[0007]   Therefore, it is also desirable to have pulsed chemical reactions that generate the highest possible peak power and peak reaction rates to produce hot electrons.

[0008]   A problem associated with pulsed chemical reactions is initiating and sustaining the reactions. The problem becomes more severe when the reaction occurs near a surface, e.g., a conducting surface, and the reaction is confined to a small volume, e.g., when dimensions of the confining volume are the order of a micron or less.

[0009]   In a typical reaction chamber, the energy of reactions is contained in and by the gas and contributes to sustaining the reaction above ignition. In such chambers, the reaction is sustained or maintained in part because reaction intermediates called autocatalysts are created and consumed by the reaction.

[0010]   In a small reaction region, however, sustaining or maintaining the reaction becomes problematic. For example, in a small reaction region, any electromagnetic energy generated radiates promptly out of the small reaction region because of the extremely high surface to volume ratio of the small, micron-size region. Further, translational and vibrational energy of autocatalysts and reaction products created as a result of the reactions is quickly dissipated upon contact with the reaction chamber walls. The energy generated in smaller volumes, therefore, do not contribute

significantly to sustaining the reaction.

[0011]   In small reaction volumes, e.g., with dimensions in the order of one micron, the burst of reactions is a transient phenomenon that is extinguished when the reactions deplete the autocatalysts. These auto-catalysts, which are generated during the reaction, play a key role in sustaining the reaction. One micron is the size of approximately two diffusion lengths for vibrationally excited byproducts of a typical fuel-air reaction during their 10 nanoseconds lifetime after initiation. The vibrationally excited species thermalize during this time. This diffusion length is typically longer than the translational mean free path and is a function of the lifetime of the vibration state.

[0012]   Fast depletion of the energy of reaction tends to extinguish the reaction. Reactions such as fuel-oxidizer reactions are maintained by the creation of autocatalysts. The autocatalysts are consumed by reaction with the fuel and oxidizer and are produced as a result of the reactions. Keeping or raising the gas temperature above the ignition temperature serves to create the autocatalysts.

[0013]   The autocatalyst are typically free radicals that are known to sustain a reaction and rapidly drive the reaction to completion. Therefore, it would be advantageous to have a method to insert the autocatalysts into the reacting mixture. By introducing more autocatalysts in the reaction, the reaction can be sustained beyond its natural tendency to deplete energy and become extinguished.

[0014]   The byproducts of a reaction in the small reaction region are initially created in highly vibrationally excited states of gas molecules. It has been observed that vibrationally excited species may collide between hundreds or thousands of times with other specie in the gas before the energy is dissipated into the gas, such as into translation and rotation modes. If, e.g., a vibrationally excited state would take about 100 collisions to thermalize, the lifetime would be in the order of 10 nanoseconds. When such vibrationally excited species diffuse through the gas and contact a metal surface, it has been demonstrated that they may transfer a major fraction of their energy during a single collision with the surface and in the form of a hot electron. This electron energy transfer may also take away energy from the reaction in the small reaction region forming a micro volume, and deny the reaction the energy needed to

maintain the temperature of reaction. Instead, the energy denied to the reaction is transferred to the surface.

[0015]   These forms of transferred energy, e.g., radiation and hot electrons, may be collected using semiconductor devices. The same semiconductor devices may also convert the energy into more useful forms such as electricity.

[0016]   It is well known that the reaction surface chemical reactivity increases almost exponentially with increase in temperature. It would be highly desirable to have only the reaction surface reach the high temperature, so that only minimum amount of heat is used to raise the reaction surface temperature.

[0017]   It is also desirable to have the thinnest possible reaction surface that switches to a high temperature for a short duration, and to have the reaction surface reach this temperature when the reactants are in contact with the reaction surface. Further, to efficiently stimulate and generate energy, it is desirable to concentrate the energy used to heat the reaction surface into pulses. Yet further, it is desirable to initiate reactions in pulses.

[0018]   Molecules collide with the device"s surface and also produce a pulse of heat. This pulse of heat, injected into the device surface, is transient and therefore, the device may dissipate the heat into the device"s volume over time. In this way, the device operates at its average temperature, not the peak temperature of the reaction. This mode operation reduces or eliminates high temperature that would normally cause the device to run inefficiently.

[0019]   A pulse of one electron volt hot electrons lasting under 500 femtoseconds, when injected into a thin metal conductor by any one of many known external means may concentrate the electron energy in the conductor surface electrons as a result of the hot electron transfer. This concentration raises the temperature of the surface electrons to exceed approximately 5,000 Kelvin within approximately one picosecond and forms hot electron gas. The hot electron transfer and the raising of the temperature occur in a conductor having a dimension of order of the diffusion length for 1 eV hot electrons. This diffusion length is in the order of 10 nanometers, which is typically 30 molecular or atomic layers thick.

[0020]   It has been shown that this hot electron gas may react within picoseconds with any chemicals adsorbed on the surface of the conductor, thereby driving reactions which may even be inaccessible to thermal processes.

[0021]   It has been shown that the 5,000 Kelvin or hotter electron gas couples to the metal vibrations, also referred to as phonons, to raise the temperature of the phonons to the order of 2,000 Kelvin over a similar dimension of surface and over a time period of 1–3 picoseconds. The phonons move more slowly than the electrons, and therefore dissipate their energy to and equilibrate with the bulk material over time periods typically of order 50 picoseconds.

[0022]   The result of the hot electron pulse is a metal surface with an effective temperature far exceeding that of the bulk, and advantageously, a reaction surface with activity associated with the peak temperature. This high temperature may persist until the phonons couple the energy to the bulk, i.e., for about 50 picoseconds, which is the time the phonons take to couple their energy to the bulk.

[0023]   Further, when there is a catalyst surface with temperature exceeding thousands of degrees Kelvin, adsorbates on that surface may promptly react or dissociate, and free radical specie and translationally hot atoms or molecules may readily and promptly desorb into the region near or on the reaction surface. Such free radicals and energetic specie are known to be autocatalytic and necessary for initiating and sustaining chemical reactions, such as combustion.

[0024]   A known method to create a hot electron pulse in the surface uses femtosecond lasers. While such lasers create a short pulse, they are typically laboratory sized and cannot be reduced to micro-chip dimensions.

[0025]   Flashlamps driven by pulsed electrical discharges are another known way to create and inject free radicals into a reactive chemical mix to initiate reactions. These fast flashlamp methods of causing electrical discharges, however, typically yield pulses no shorter than 5 to 10 nanoseconds, and require kilo-volt initiator and switching systems. Further, the flashlamps will only cause significant hot electron generation in the conductive surface and not in micron-sized volume of reactants. Thus, such flashlamps typically render optical stimulation inefficient.

[0026]   Therefore, it would be highly desirable to have a method and device that provide a burst of hot electrons into nanometer dimension surfaces efficiently, and during the time before the phonons of the thin reaction surface reach equilibrium with the bulk.

Summary of Invention

[0027]   The present invention is directed to stimulating pulsed chemical reactions in a micro-volume containing gaseous reactants. A highly useful application includes but is not limited to generating electricity. Other applications include energizing a light emitting diode, energizing a laser diode, electrically energizing a quantum well, energizing a quantum well using phonons, and energizing chemical reactions with transported hot electrons and hot carriers.

[0028]   In one embodiment, an emitter stimulates the reactions of a fuel-oxidizer mixture and a collector converts the high level of molecular vibrational energy of the resulting products directly into electricity.

[0029]   The device of the present invention to stimulate and collect energy may be configured in many ways. In one embodiment, the device includes an emitter that stimulates and initiates the reactions in the reactant mix, a reaction region, a collector, and reactants such as fuel and oxidizer.

[0030]   The emitter acts like a spark plug and may be constructed to be on the same surface as the collector, to be the same physical device as the collector, or to be on the same surface of a contoured surface including the collector. The fuel may be mixed with oxidizer or may be separately injected. The emitter may be insulated from the collector and may be on separate structures distinct from the collector. The reaction region may be completely enclosed or partly enclosed by collectors or it may be open to reactant flow. The reaction region may include the surface of the collector itself. The reactants may adsorb or partially adsorb on the collector and on the emitter. More than one type of fuel or oxidizer may be provided, e.g., one type of fuel mixed with one type of the oxidizer and the other fuel, another oxidizer or mixture separately injected.

[0031]   In one embodiment, the device is formed on and hewn out of a substrate semiconductor to form both the emitter and the collector . The device includes a

collector which includes a diode, an emitter, and a reaction region. In one embodiment, air, including exhausts, is made to flow into and out of the reaction region, and fuel is made to flow into the reaction region. The device may be configured in several geometries, including but not limited to, a V-channel, a box, and a plane.

[0032]   In one embodiment, to cause the reactivity of reaction surface to switch to its high temperature value and become active, a thin, tens of nanometers or less dimension or thickness of the reaction surface is heated during a pulse. The reaction surface may comprise a catalyst surface. The switching feature permits the choice of catalyst material to include materials not normally considered to be catalysts.

[0033]   The reaction surface may be part of either or both the emitter and collector. Reactants may "plate-out" in the sense of adsorbing on a reaction surface, thereby concentrating the reactants on a reaction surface. Plate-out may be enhanced by choosing material for the reaction surface with high sticking coefficient for fuel, oxidizer, or both. For example, sticking coefficient in excess of 0.05 may be useful for plate-out. The concentrating may provide conditions for high peak reaction rates and high instantaneous peak power. The adsorbing process includes incomplete adsorption, e.g. adsorption into precursor states.

[0034]   A sudden onset of high reactivity of the reaction surface causes a sudden production of and to some degree desorption of autocatalytic material, resulting in stimulation of reactions in the gas next to or on the reaction surface. In one embodiment, an initiation is supplied, where the initiation of chemical reaction between fuel and oxidizer is prompt, for example, taking tens of picoseconds, and causes the sudden onset of this high reactivity between fuel and oxidizer.

[0035]   In one embodiment, a pulse of energy such as hot electrons, photons, or phonons, are created and injected into a thin reaction surface. The pulses may originate as optical or electrical pulses. The duration of the pulse is, e.g., shorter than the time it takes for phonons in the surface in contact with the reactants to equilibrate with the substrate .

[0036]
         In one embodiment, hot electrons are injected into the thin, nanometers-thick

conductive layer to heat the electrons of the conductive layer. This method preferentially heats the electrons faster than heating the vibrations of the conductive layer. The vibrations are heat; the heated electrons are useful. This preferential heating of electrons occurs because the heat capacity of electrons is orders of magnitude lower than that of atomic vibrations, so a given energy input heats them orders of magnitude hotter than vibrations.

[0037]   In one embodiment, the preferential heating of electrons in the conductive layer may be further enhanced by choosing the thickness of the conductive layers to be of the same order of magnitude or less than the energy diffusion parameter of the electrons, which thickness is of order 10 to 50 nanometers.

[0038]   In one embodiment, chemical reactions produce exhaust products which desorb from reaction surfaces, thereby permitting further chemical reactants to replenish their supply on the surface.

[0039]   In one embodiment, catalysts accelerate the replenishment of reactants on a reacting surface.

[0040]   In one embodiment, rapid replenishment of reactants permits sufficient power density to maintain a useful voltage across the collector diode, with associated useful power output. The collector diode may include a Schottky diode or a p-n junction diode.

[0041]   In one embodiment, the collector may include a unipolar device, such as a quantum well, where excitations such as phonons, longitudinal optical phonons, and electrons, may energize the unipolar device. The reactive surface of such a collector may include materials and practices tailored to cause a predominance of phonons to energize the device or to cause a predominance of electrons to energize it. Such tailoring may include tailoring the quantum well levels. Such tailoring may also include choice of material Debye temperature, the use of superlattices, and tailoring of the phonon and electron band structure of superlattices.

[0042]   Further features and advantages of the present invention as well as the structure and operation of various embodiments of the present invention are described in detail below with reference to the accompanying drawings. In the drawings, like reference

numbers indicate identical or functionally similar elements.

Brief Description of Drawings

[0043]   Preferred embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings in which:Figure 1 shows a schematic cross section of a gas-phase-reactant-pulsed electric generator using a reaction stimulator in a V-channel geometry in one embodiment; Figure 2 shows the device having a box structure;Figure 3 shows a top view of a gas-phase-reactant, pulsed electric generator using a reaction stimulator in either flat or V-channel geometry;Figure 4 shows a schematic top view of a gas-phase-reactant-pulsed electric generator using a reaction stimulator in either a flat or a V geometry with a single fuel port; Figure 5 shows a gas-phase-reactant-pulsed electric generator with emitter surrounding the collector; Figure 6 shows a schematic cross section diagram of gas-phase-reactant-pulsed electric generator using a reaction stimulator in a box geometry with a fuel port;Figure 7 shows a transmission line used to drive the injector of the device of the present invention in one embodiment;Figure 8 shows an example of composites placed in direct contact with the injector in one embodiment; andFigure 9 shows a transmission line used to drive an emitter injector that is also a collector.

Detailed Description

[0044]   Figure 1 shows a schematic cross section of a gas phase reactant, pulsed electric generator using a reaction stimulator in a V-channel geometry. Fuel and air mixture diffuses into the V-channel from above the V-channel. The emitter includes an electrically-driven hot electron generator, the hot electron generator also being referred to as an injector, such as a metal-insulator-metal (MIM) injector or a metal-semiconductor-metal (MSM) injector. The injector includes an electrode 107 formed on a structure 110, e.g., a heat insulator. In MIM injector a thin tunneling insulator 108 is used to provide hot electrons and a thin reaction surface 109, which also may be an electrode, is activated by the injector 108.

[0045]   In a MSM version a semiconductor 108 is used to provide hot electrons. A thin reaction surface 109, which also may be an electrode, is activated by the injector 108. The reaction surface and electrode 109 of both versions MSM and MIM may use layers and clusters of catalyst and layers and clusters of insulator or other material arranged

on a metal or conducting substrate, shown as a single element 109.

[0046]   A pulse of hot electrons is created by applying an electric pulse across the injector electrodes 107, 109. This pulse of hot electrons is injected into the thin reaction surface and electrode 109. The duration of the pulse, e.g., is shorter than the time it takes for phonons in the reaction surface 109 to diffuse away from the thin reaction surface 109. This pulse duration is typically less than 50 picoseconds and greater than 10 picoseconds. Electrical pulses, e.g., may be of duration approximately 30 picoseconds to energize an emitter 107, 108, 109. The length of the pulse is an engineering parameter that depends in part on the degree of phonon isolation or impedance mismatch between the reaction layer 109 and substrate injector 108.

[0047]   In Figure 1, injector is shown as an insulator layer 108 placed between two electrodes 107, 109. The injector also may be, but is not limited to, any one of the following devices: a forward biased diode, a metal-insulator-metal device, a semiconductor-insulator-metal device, a semiconductor-metal device, an optical device, or a quantum well. These injector devices produce a common effect, i.e., the generation of hot electrons and insertion into a thin reaction surface with, e.g., sufficiently thin dimension to render the hot electrons useful.

[0048]   The electrically driven forms of the emitter include electrodes such as those shown in 107 and 109, and a reaction surface 109. In one embodiment, the reaction surface 109 and the electrode 109 may be one and the same.

[0049]   In one embodiment, to energize the injector electrodes 107 109, stored electric charges are switched into or injected into the injector 107 108 109. This switching causes a forward bias in the diode or injector, further causing the stored charges, in the form of hot electrons, to be dumped into the thin conductive metal electrode 109 which may also be a reaction surface. These dumped hot electrons desirably heat the electrode 109 and the reaction surface. In Figure 1, the reaction surface is shown as the same element as the electrode 109.

[0050]
     In one embodiment, the electrical pulse may be achieved by electrically driving a transmission line or strip transmission line, also referred to as a stripline. This is schematically shown in Figure 7. Figure 7 shows a stripline superimposed on, e.g., the

device of Figure 1. The electrical pulse is achieved by driving the stripline at one end with an electrical pulse across electrodes 700 and 701. The stripline includes electrodes 700 and 701 and dielectric material 702. The pulse travels from input electrodes 700 and 701 to output electrodes 703 and 704. This stripline is a waveguide. By constructing what is called a dispersive waveguide, by proper choice of dielectric and electrode properties and configurations, a pulse may be narrowed. This transmission line terminates with its electrodes 703 and 704 by connecting to the injector electrodes 707 and 709.

[0051]   Referring back to Figure 1, when the hot electron injector is designed to be a tunneling insulator, the dimensions of the tunneling insulator 108 and thin reaction surface 109 are chosen to be of order the same size or less than three times the energy diffusion length of the hot electrons traversing the insulator 108, which dimension is e.g., of order tens of nanometers or less in the metal. The term diffusion length of hot electrons refers to the diffusion length of electrons with the energy appropriate for their use. E.g., a hot 1 eV electron may degrade into several 0.1 eV electrons. The diffusion length for 1 eV electron in a metal is typically shorter than that of 0.1 eV electron . Under some conditions the diffusion length of an electron in a metal scales as the square of energy relative to the Fermi level energy.

[0052]   In one embodiment, the electrode 109 that receives the hot electrons is formed to be thin with dimensions typically of order less than three diffusion lengths of hot electrons. These electrodes that receive hot electrons may include but are not limited to any one or combination of a diode, a metal–insulator–metal device, a metal layer, a metal layer on a semiconductor, and a quantum well. These variations of emitter configurations describe different ways to create hot electrons and render them useful at a reaction surface.

[0053]
          In another embodiment, optical pulses may be applied to energize the injector. In this case, the injector electrode 107 would not be needed. A similarly thin conductor 109 and an optically thick semiconductor 108 are used to receive optical energy generated by an external optical generator device. Any known optical generator device may be utilized. An electrode formed from the thin conductor 109 on the semiconductor 108 absorbs the optical energy and creates hot electrons. These hot

electrons migrate to the reaction surface 109.

[0054]   In another embodiment, the reaction surface 109 is formed with composites or layers, e.g., an underlayer of conductor with dimension less than two diffusion dimensions for hot electrons, and coated with a similarly thin layer of a desirable catalyst. Any desirable catalyst may be used. Such composites or layers may be in direct contact with the electron injector element (Figure 1, 107, 108, 109).

[0055]   An example of composites placed in direct contact with the injector is shown in Figure 8. The composite includes a layer of conductor 801 such as RuO_2 with average thickness of order 10 nanometers or less, under a catalyst layer such as gold or platinum with thickness about 10 nanometers or less. Another example of catalysts includes an alumina spiked with vanadia or other catalysts. When an electrical pulse of order volts is applied to the electrodes 107 and 109, the fuel and oxygen adsorbed on the emitter 109 802 is partially reacted into free radicals or reacted, and desorbed and delivered into the reaction volume. The reaction volume is shown in Figure 1 as the V-shaped channel region between the conducting surface 106 and the injector 107, 108, 109. The chemical reactions occur in this V-shaped channel region or on the reaction surfaces in contact with this regionThe vibrationally excited reaction products may deposit a substantial fraction of their vibrational energy into an electron of a conducting surface 106, producing one or more hot electrons. The reaction products may also include, but are not limited to, photons, vibrationally excited molecules, and free radicals.

[0056]   The catalytic reactivity with respect to reactions occurring on the reaction surface 109 (Figure 1) or 802 (Figure 8) includes the reactivity associated with the presence of hot electrons on a surface. Recent experiments have demonstrated that such hot electrons with temperatures of order 5,000 Kelvin and above have altered the reaction kinetics of adsorbed species. Experiments showed that hot electrons caused vibrational excitation of the adsorbate species. Experiments showed that as a result of the energy imparted to the adsorbates by the electrons, reactions proceeded along paths inaccessible via thermal means, including highly endothermic reactions.

[0057]   The dimension of the channel from the emitter to the collector defined by a region measured approximately from the geometric center of the cross section at electrode

109 to the center of the collector surface 106 is of order less than three times the energy diffusion length of vibrationally excited reaction products resulting from reaction initiation. This length is of order ½ to 1 micron at standard temperature and pressure (STP) conditions.

[0058]   The collector 106 provides a conducting surface, with thickness dimension sufficiently thin to permit the hot electron to travel through the electrode 105 of the collector and into the highly doped p+ region of the semiconductor 104. The internal field produced by the p+ region 104 and p doped region 103 of the semiconductor tends to draw the electron to the p region 103. The stronger electric field produced by the junction of the p region 103 with the n doped semiconductor base 111 draws the electron over the diode junction. This diode junction is the interface between the p region 103 and the n region 111. In this manner, the diode that includes the p region 103 and n region 111 becomes forward biased, producing a useful voltage across the electrodes 102 and 112. The positive electrode 102 is connected to the diode electrode 105 and isolated from the diode base 111, e.g., n doped semiconductor base, by an insulator 101.

[0059]   The thickness of the base semiconductor 111 may be chosen according to engineering needs. The thickness or height of the structure 110 supporting the emitter may similarly be chosen and may include raising the emitter more into the V-channel, e.g., one third of the way up from the bottom of the V-channel.

[0060]   Referring to Figure 8, the input of hot electrons into the thin, nanometers-thick conductive layer 109 or into layers 801 and 802 heats the electrons of the conductive layer faster than heating the vibrations of the conductive layer. This heating of electrons over atomic vibrations is enhanced by choosing the thickness of the conductive layers 109, 801, 802 to be less than about two times the energy diffusion parameter of the electrons, which thickness is of about order 10 to 50 nanometers.

[0061]   The choice of materials of the conducting layers 109, 801, 802 may also enhance the heating of electrons. E.g., choosing materials with differing sound speeds, or with mismatched phonon band frequencies may result in more efficient confinement of electron energy. Such choices of materials further enhance thermal isolation and confines the energy in the electrons.

[0062]   The choice of structures may enhance the confinement of hot electrons. E.g., placing the conducting layers 109, 801, 802 on pillars, nano-bridges or otherwise raised structures may also produce more efficient results for electron heating. Structures including a small number, e.g. less than 50, of monolayers of dissimilar conductors, e.g. silver layers on nickel and platinum layers on gold, forming quantum confinement of electrons, may also enhance hot electron confinement.

[0063]   In one embodiment, pulsed hot electron injection device 107, 108, 109 (Figure 8) deposits externally supplied energy in the conductive layers 109, 801, and 802.

[0064]   The hot electron injection device energizes the chemicals adsorbed on the emitter surface and makes them act like a spark plug, triggering reactions in the gas surrounding the trigger or adsorbed on the trigger. The emitter operation starts with some energy source creating hot electrons in an injector. The injector conveys the hot electrons to chemicals adsorbed on the reaction surface. Hot electrons interacting with chemicals cause chemical reactions. Hot electrons also case physisorbed adsorbates on a reaction surface to become chemisorbed or desorb, and may also cause chemisorbed adsorbates to dissociate on the reaction surface or to become physisorbed or desorbed. Some reactions form autocatalyst chemicals, which are highly reactive chemicals. Some reaction products desorb from the reactive surface. The desorbed reaction products typically possess sufficient excess kinetic energy to initiate reactions in gas molecules. Desorbed products typically include autocatalysts which are necessary to sustain chemical reactions such as burning and combustion.

[0065]   An example of one energy source creating hot electrons is an applied voltage across an insulator or semiconductor. Another example of an energy source is a light source, such as a flash lamp or a pulsed laser beam.

[0066]   A pulsed hot electron injector may deposit the energy in a time that is so short that the hot electron energy deposits entirely in a nanometers thin reaction surface, heating it to effective temperatures of thousands of degrees Kelvin. This short duration, high intensity pulse of energy switches the reaction surface from an inactive or non-catalyst state to a highly reactive catalyst state.

[0067]
     The electrons alone may be heated to thousands of degrees. The characteristic

time for this is of order 0.5 picoseconds. The phonons or vibrations are heated by the electrons, with characteristic times of order 1 to 3 picoseconds. The phonons dissipate into the lattice with characteristic phonon diffusion times of order 30 to 50 picoseconds.

[0068]   The pulse duration of the pulsed hot electron injector, therefore, may include the use of devices that produce energy pulses such as optical or electrical pulses with durations of order less than the phonon diffusion time in the target conductive layers. The energy pulses such as optical or electrical pulses impinging on the conductive layers 109, 801, 802 create the pulse of hot electrons.

[0069]   A pulsed hot electron injection device of this invention includes the use of devices that produce either optical or electrical pulses with durations of order less than the phonon diffusion time in the target conductive layers. A method of the invention includes using the optical pulse impinging on a conducting surface 109 to create the pulse of hot electrons. A method of the invention includes using an electrical pulse to drive a semiconductor device or a metal-insulator-metal device 108 designed to inject or transport hot electrons into its positive electrode 109 801 802 and to drive hot electrons from the electrode into the reacting surface 109 802.

[0070]   The method includes using an optical source of photons as the primary source of energy to create hot electrons. The optical photon energy shall be sufficient to create hot carriers in the semiconductor 108 conduction band. The subsequent diffusion of carriers drives hot electrons into thin conductive layers 109 801 802 on a semiconductor substrate.

[0071]   yyyyy1yyyyy1In one embodiment, the injector includes a semiconductor 108 which creates hot electrons from absorption of light from an external optical source. In this embodiment, an optical source with photon energy to create carriers in a semiconductor substrate 108 may be used to irradiate that semiconductor 108 and create hot electrons in its conduction band. The hot electrons so created in semiconductor 108 rapidly, e.g. within tens of picoseconds, diffuse into the reactive surfaces 109, 801, 802.

[0072]
       The semiconductors used in the present invention may include those with either

direct or indirect band gaps. The lifetime of the created hot carriers in the semiconductors with indirect band gaps may be as long as microseconds. Examples of such semiconductors with indirect band gaps include but are not limited to silicon (with band gap of order 1.12 eV), germanium (with band gap of order 0.66 eV), PbTe (with band gap of order 0.31 eV), and PbS (with band gap of order 0.41 eV).

[0073]   In semiconductors with direct band gaps, the mobility of the created hot carriers may be high compared to other semiconductors. The band gap in such semiconductors may be engineered. Examples of such semiconductors with direct band gaps include but are not limited to In-x Ga-y As-z Sb-w, where the band gap can be adjusted over a range including 0.1 eV through 1.5 eV. The x, y, z, w values represent the fractional concentrations of each element.

[0074]   The hot electrons created in the underlying semiconductor 108 that move into the conductive overlayer 109, 801, 802, i.e., a reaction surface 109, 801, 802, may become trapped on the reaction surface 109, 801, 802 because the hot electron lifetime in the surface is less than tens of femtoseconds, which is orders of magnitude shorter than the lifetime in the semiconductor. A hot electron in the substrate 108 has a very long life time by comparison and may diffuse through the semiconductor 108 for times exceeding many picoseconds and ranging even to microseconds. The hot electron inevitably diffuses into the conductive overlayer 109, 801, 802.

[0075]   To achieve this diffusion, a pn junction semiconductor with the p side ohmically or almost ohmically attached to the reaction surface 109 may be used. The semiconductor 108 may include an n type semiconductor at the junction with the electrode 107 and become and formed to be p type at the other electrode 109.

[0076]   The novel feature of the device includes the ohmic or almost ohmic contact with the valence band and demonstrates the desirable property of conveying the full, conduction band electron energy into the reaction surface 109.

[0077]
           In one embodiment, a Schottky diode may be used. Gold and platinum form desired Schottky junctions with silicon, and therefore, may be used to form a hot electron injection diode. Gold has the longer hot electron diffusion length, and therefore, may be more desirable in some applications. Platinum has the higher

catalytic activity, and therefore, may be more desirable in other applications. E.g., gold nano-structures have been shown to catalyze the reaction of CO with oxygen, while platinum has been shown to catalyze the reaction of ethanol and methanol with oxygen, and both at temperatures within the operating range of silicon, i.e., less than 370 degrees Kelvin.The RuO_2 or alumina-oxide-metal reaction layer 801, 802 may be deposited on the conductive contact 109 of the metal-silicon Schottky junction 109, 108 as shown in Figure 8, where the conductor thickness is less than three times the diffusion dimension of hot electrons surmounting the Schottky junction 108-109, and where the conductor 109, 802 is selected for convenience.

[0078]   In one embodiment, the pulse of hot electrons heats the metal 109 of the Schottky junction and hence heats the catalysts 801, 802, e.g., RuO_2 or spiked alumina, causing the catalysts to become highly reactive. Nearly all metals may form a Schottky junction diode with silicon.

[0079]   An electrical pulse forward biases the diode 107, 108, 109, with the negative terminal 107 connected to the semiconductor and the positive terminal 109 connected to the diode conductive electrode 109. This diode uses an n type semiconductor with a conductive electrode 109. The electrode 109 is biased positive and the semiconductor 108 is biased negative. The conductive electrode 109 and any conductor 801, 802 on top of it is formed with dimension of order less than three diffusion lengths for hot electrons.

[0080]   Upon switching the electrical pulse into electrodes 107 109, the hot electrons surmounting the diode Schottky barrier then flood the positive thin diode conductive electrode 109 with a pulse of hot electrons. The hot electrons equilibrate with the electrons in the electrode 109 and raise the instantaneous electron temperature.

[0081]   Similarly, in an embodiment having an electrically pulsed pn junction diode 107 108 109, the electrical pulse forward biases the diode. In this embodiment, the p side of the semiconductor is faced towards the reacting surface 801 802. An electrical contact 109 is formed to the p type semiconductor so that the conducting electrode forms an almost ohmic junction. Composite catalysts 801 802 are formed in contact with the electrical contact as the reaction surface.

[0082]   In an emitter embodiment having electrically pulsed metal-insulator-metal junctions or semiconductor-insulator-metal junctions for injector, the conductive layer receiving the electrons that cross the insulator 108 is formed similarly thin, e.g., with dimension of order less than three diffusion lengths for hot electrons. In this embodiment, the electron transport may be via tunneling through the insulator 108, passing through its conduction band. Transport may be also via electrons with energy greater than the Schottky barrier. The transport may be resonant with adsorbates on the reactive surface can be enhanced by choice of adsorbates through choices of fuel, oxidizers, and additives.

[0083]   In one embodiment, electrically pulsed, solid state optically emitting diodes deliver up to 30 picosecond duration pulses of photons to a conductive surface. The diodes may illuminate the surface from behind, through substrates transparent to the radiation emitted by the diode, e.g., as appropriately chosen material 111 108. E.g., a diode emitting 1 eV photons in the infra-red may pass through materials 111 with 1.5 eV or larger bandgap. Such materials include GaAs, alumina, or insulators.

[0084]   In one embodiment, the electrically pulsed solid state optically emitting diodes deliver pulse compressed optical radiation, using e.g., chirped pulses compressed using dispersive media.

[0085]   In one embodiment, pulses are chosen to have durations less than approximately 10 to 50 picoseconds, depending on injector and reactive surface material thermal conductivity and energy transport properties. This duration is approximately the time for the energy deposited by the electrons to migrate via phonon heat conduction from the reactive surface into the underlying injector material 109.

[0086]   Commonly available 30 GHz transistors, radio frequency pulse generators, magnetic, electrical storage, and pulse compression systems may be used to produce pulse durations satisfying the criteria of less than 10 to 50 picoseconds pulse durations. These generators include power signal generators typically used to generate millimeter waves, e.g., those used in satellite communication or in radar pulse generation. Such power signal generators include gun diodes, vacuum tube devices, klystrons, magnetrons, and any of many devices currently available to generate pulses with duration less than approximately 50 picoseconds.

[0087]   In one embodiment, the pulsed electric generator of the present invention includes the emitter 109 801 802, the energy collector 101 102 103 104 105 106 111 112, and a reaction volume, which is the region between the emitter and the energy collector. In one embodiment, the emitter may be an integral part of the collector. In another embodiment, the emitter and the collector may be the same physical device.

[0088]   E.g., a semiconductor diode energy converter may be operated in the reverse mode to provide hot electrons to its surface, which may render it an emitter. An advantage of an integral emitter and collector is simplicity of design. A pulse applied to the emitter initiates reactions and the reactions in turn generate electricity in the collector. Thus, the same device may initiate reactions and collect energy. The result is the equivalent to stimulating a negative resistance.

[0089]   In another embodiment, an emitter and a collector may be separate. Having a separate emitter and collector allows the two to operate at different temperatures. E.g., the collector may include semiconductor devices that operate more efficiently at lower temperatures. The emitter may not require the use of temperature sensitive semiconductors, and may operate at higher temperatures for more efficiency.

[0090]   Referring to Figure 7, an initiator pulse is sent into a transmission line 700 701 702 to emitter electrodes 707 709. When the emitter is also a collector and because of the pulsed reactions a pulse with more energy than the initiator pulse is received into the transmission line from the collector.

[0091]   The transmission line may also connect to collector electrodes. The emitter and collector may be the same physical device. Referring to Figure 9, an initiator pulse sent into the transmission line 900 901 902 propagates to its output electrodes 903 904 and energize emitter electrodes 101 112. The emitter and collector electrode may be one and the same. However, the emitter stripline may be distinct from the collector output system.

[0092]   Figure 2 shows the device having a box structure. For descriptive purposes only, the device is shown isolated and standing alone. In practice, a base semiconductor 8 is used to hew boxes 200, resulting in an array of the boxes 200 stacked next to one another. E.g., a another of the semiconductor base 8 may form an adjacent wall.

[0093]   The fuel is injected or diffused into the reaction region from the bottom of the device and air diffuses from the top. The collector, emitter, and reaction region elements of this device are similar to those of shown in Figure 1. The collector 1 forms the inside walls of the box formed out of the semiconductor 8. Fuel port 2 allows fuel to enter the reaction region inside the box.

[0094]   Having the fuel enter the reaction region inside the box permits direct evaporative cooling of the semiconductor 8. Direct cooling of the device precisely at the point where heat may be generated and is a novelty of the configuration and permits higher power operation at a given average temperature.

[0095]   The box geometry is also appropriate when fuel and air are fed to the device premixed. In this case the fuel port 2 may be used to feed both fuel and air, or to feed alternate fuels and oxidizers, or as a carburator, or may be eliminated entirely, depending on engineering needs.

[0096]   A fuel-rich emitter may also be advantageous. The production of autocatalysts may be greatly enhanced by providing the emitter with a set of chemicals that readily dissociate and preferentially produce autocatalysts upon hot electron stimulation. In this case, the fuel port may serve instead as the port for such additives, such as fuels and/or oxidizers. This may also serve to permit lean mixtures of fuel and air, which may also provide a cleaner reaction.

[0097]   The emitter 3 is energized by emitter electrodes 4 6 and initiates the chemical reaction between fuel and oxidizer. Collisions of the vibrationally excited products with the collector wall 1 forward bias the semiconductor 8 that is connected to negative electrode 6 and positive electrode 7.

[0098]   Figure 3 shows a top view of a gas-phase-reactant, pulsed electric generator using a reaction stimulator in either flat or V-channel geometry with the fuel port 304 being adjacent to the collector. The fuel port 304 is located adjacent to the collector 303 and surrounds the emitter 302 and the electrodes 301.

[0099]   Figure 4 shows a schematic top view of a gas phase reactant, pulsed electric generator using a reaction stimulator in a either a flat or a V geometry with a single fuel port. The gas diffusion process with dimension of order of the diffusion length

for the excited state specie permits flat geometries to be nearly as efficient as enclosing geometries such as the box. Emitter 402 with electrodes 401 are shown separate from the collector 404. The reaction region is out of the plane of the drawing. The substrate semiconductor extends into the plane. The fuel emerges from the fuel port 403 from the bottom of the device and into the reaction region above the plane.Figure 5 shows a configuration similar to that of Figure 4, with emitter 502 surrounding the collector 501. In this embodiment, a fuel port 503 is located adjacent to the structure. This configuration may be repeated over the surface of the semiconductor.

[0100]   Figure 6 shows a schematic cross section diagram of gas-phase-reactant-pulsed electric generator using a reaction stimulator in a box geometry with a fuel port, and shows more detail for the geometry of the device shown in Figure 2. The collector includes negative electrode 611, n doped semiconductor 610, p doped semiconductor 609, p+ heavily doped 608, diode electrode conductor 605, collector conductor surface material 604, positive electrode 606, and electrical isolating insulator 607. Fuel enters from the bottom of the device through fuel port 612. The emitter is shown with an electrode 601 , thin insulator 602, and reactive surface 603. A structure under the emitter is omitted to show that it may be an option to omit the extra structure.

[0101]   Fuel port 612 is shown entering in close proximity to the emitter 601, 602, 603, to suggest the option of a fuel rich ignition region and the feature of a cooling of the semiconductor 610 closest to the hottest element, the emitter.

[0102]   In one embodiment of the present invention, semiconductor diodes are used to collect and convert photons into electricity in addition to the hot electrons. E.g., a thin conducting surface is used to convert the energy of vibrationally excited molecules into hot electrons. The semiconductor diodes are then used to convert the both the photons and the hot electrons into a forward bias across the diode, which generates electricity.

[0103]   Many geometries of emitter, reaction region, and collector may exhibit useful efficiencies and features. In one aspect, a spherical collector surface encloses a spherical reaction volume with a point emitter in the center, with the radius of the sphere less than three diffusion lengths for vibrationally excited specie. The

semiconductor outside the sphere is used to form the collector diode. Fuel and air enter through holes or ports in the semiconductor. Exhaust leaves the system through ports, holes, or channels in the emitter at the center of the sphere, for example through a tube or pipe from the center to outside the sphereThe emitter may operate at an higher temperature than the collector. In one embodiment, the reaction volume is enclosed in a box with one end open to reactant and exhaust flow. The emitter structure is placed in the center of the box as shown in Figure 2 and Figure 6.

[0104]   In one embodiment, the emitter (Figure 6 601, 602, 603) in the present invention may include a reaction surface to receive and use hot electrons and an injector (Figure 6 601 602) that generates and provides the hot electrons. The reaction surface (Figure 6 603) includes a conductor and may optionally include layers of material. The layers of material may include conductors.

[0105]   The injector produces the hot electrons and injects them into the reaction surface. This injector may include but is not limited to any one or combination of the following devices: Schottky diode; pn junction diode; metal-semiconductor-metal device; metal-insulator-metal device; semiconductor-insulator-metal device; quantum well; optical generator where the optical radiation impinges directly on the thin conductive reaction surface from behind or from the front; optical generator where the optical radiation impinges on a semiconductor, creating hot carriers in the semiconductor which migrate to a similarly thin conductive electrode surface.

[0106]   When the injector, i.e., hot electron producer, 107 108 (Figure 1) is a Schottky diode, the semiconductor provides electrons that surpass the Schottky barrier and travel from the semiconductor 108 into the conductor 109 that forms the electrode 109 of the diode. The electrode 109 and any materials 801 802 (Figure 8) on the electrode form the reaction surface.

[0107]   When the injector is a pn junction diode, the p type semiconductor provides electrons from its conduction band. The electrons in this embodiment are minority carriers that travel into the ohmic or almost ohmic electrode 109 and come in contact with the valence band of the p type semiconductor 108. The electrode 109 and any materials 801 802 on the electrode form the reaction surface.

[0108]   When the injector is a metal-semiconductor-metal or metal-insulator-metal device, one metal 107 is biased negative and the other metal 109 is biased positive. Electrons originating in the one metal 107 travel through the metal-insulator or metal-semiconductor layer 108 and are driven into the other metal 109, biased positive, appearing as hot electrons in the metal 109 . The electrode biased positive and any materials 801 802 on the electrode form the reaction surface.

[0109]   When the injector is an optical generator where the optical radiation impinges directly on the thin conductive reaction surface 109 either from behind or from the front, then the impinging creates hot electrons. The conductive reaction surface 109 has thickness dimension of order less than approximately three diffusion lengths for hot electrons. The thin conductive reaction surface and any materials 801 802 on the electrode form the reaction surface. When the injector is an optical generator where the optical radiation impinges on a semiconductor, the impinging creates hot carriers in the semiconductor 108 which diffuse to an appropriately thin conductive electrode surface 109. The electrode may or may not be deliberately biased using external energy sources. The electrode and any material 801 802 on the electrode form the reaction surface.

[0110]   Any known method may be used to energize the injector that generates a pulse of hot electrons. These methods include but are not limited to using devices such as gyrotrons, microwave power sources, and regenerative solid state devices. The regenerative devices include pnpn and npnp thyristor-type devices. These types of devices include light emitting diode stimulated Zener breakdown stimulators/accelerators, stripline pulse compression methods, optical pulse compression methods, tunnel diode, and resonant transfer devices, Gunn diodes, nano-triodes, and nano-vacuum tube systems.

[0111]   These energizing devices may be formed integrally or separate from the injector device that drives the hot electrons into a reaction surface. The reaction surface is then heated to temperature in excess of the emitter substrate 109.

[0112]   The surface to receive hot electrons includes a conductor 109 with thickness dimension less than three diffusion lengths for hot electrons. In one embodiment, the surface 109 and the reaction surface 801 802 are part of the same element. On one

side, e.g., the side facing the element 108, electrons may be generated and on the other side, e.g., the side facing the reaction volume containing the fuel and oxidizers, chemical specie impinge on the surface 109 801 802 and adsorb, react or otherwise interact. The thickness dimension is measured from the side facing reacting gas or materials to the side interfacing with the injector 108. This dimension is generally designed to be less than three times the diffusion length for hot electrons. E.g., this dimension is of order 10 nanometers or more for gold, silver, and aluminum.

[0113]   In one embodiment, an optical pulse may be generated using a flash lamp, electrical gas discharge, optically emitting solid state device, pulsed laser, or pulsed diode laser. The pulse of hot electrons are stimulated by dumping the charge stored in a capacitor or in the effective capacitance of a semiconductor junction.

[0114]   The pulse durations and dead time intervals are tailored to meet the engineering considerations in designing the device of the present invention, including considerations of thermal heat flow. Pulse durations and dead times may be longer than microseconds. E.g., the pulse duration for energizing is chosen so that the energy collector reaches it maximum operating temperature and then cooled down to the desired heat sink temperature during the dead time intervals.

[0115]   The dead time interval, i.e., interval between energizing pulses, is typically shorter than a time associated with the dissociation of precursors to dissociation. This interval is typically of order ten nanoseconds for oxygen on platinum at room temperature. A precursor is a trapped, intermediate form of an adsorbate as it successively surmounts activation barriers towards dissociation on a catalyst or reaction surface.

[0116]   In one embodiment, reactive species are injected into the reaction region by supplying a third specie to the emitter, e,g, a fuel catalyst or an oxidizer or a hypergolic material or a monopropellant or an initiator or reaction intermediates or autocatalysts or a mixture of these, in addition to fuel and air, to stimulate the reaction. The third species dissociate or react to form reaction stimulators. The energizing pulses cause the products of a fuel catalyst supplied to the reacting surface to stimulate pulsed fuel-oxidizer reactions.

[0117]
     The fuel catalysts may include but are not limited fuel and oxidizer mixtures,

unstable specie such as hydrazine, monomethyl hydrazine, or high explosives. The fuel and oxidizer mixtures include but are not limited to fuels such as ammonia, oxidizers such as hydrogen peroxide, or halogen oxidizers.

[0118]   In one embodiment, the reactive species are placed into a volume in direct contact with the conducting surface. The concentration of the reactive species in the volume may be adjusted so that they become depleted of reactants during the time when the system is in its dead time, e.g., by using reactive mixtures in the combustible range or using lean mixtures. Advantageously, fuels adsorb on to many catalyst surfaces as well as oxygen, so that an optimum fuel-oxidizer ratio may form on the reaction surface from a lean mixture in the gas phase in the volume. Also during the dead time, the volume may be replenished with more reactive species.

[0119]   The hot electrons and hot atoms from the products of the reaction are collected or otherwise used. The products are further used to sustain the duration of high reactivity of the reaction surface.

[0120]   The radiation emitted by hot atom reactions may be collected in the form of optical radiation. The optical radiation typically results from inverted populations such as from hot atom reactions.

[0121]   The reacting surface"s temperature is raised without raising the underlying substrate temperature above 600 Kelvin by using short reaction times and pulses. The temperature of electrons in the surface is raised to above 5,000 Kelvin, and the phonons to above 2,000 Kelvin. The temperature of the substrate is kept under a temperature that would destroy the substrate"s properties. Such temperatures are typically under 600 Kelvin. When the temperatures are kept under 600 Kelvin, a substrate would typically maintain its desirable properties.

[0122]   While this invention depicts the reaction stimulation using hot electrons, the invention also pertains to the use of hot holes. The use of hot holes entails swapping the reference to electrons with holes, swapping valence band for conduction band, and swapping positive with negative. Such swappings between electrons and holes are well known in the art.

[0123]   While the invention has been shown and described with respect to particular

embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of the invention.